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# Synthesis of Energetic Oxidizers by Radiation Techniques

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R.M. Curtis, J.N. Wilson  
SHELL DEVELOPMENT COMPANY  
A DIVISION OF SHELL OIL COMPANY

*Sponsoring Agency:*

Air Force Rocket Propulsion Laboratory  
Research and Technology Division  
Edwards Air Force Base, California  
Air Force Systems Command, United States Air Force

Final Technical Report  
April 1969 — December 1970

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The attached errata sheet, assigning the AFRPL TR No. 71-105 and showing the correct distribution statement, should therefore be made a part of this technical report.

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Errata Sheet a/s

25 August 1971

## E R R A T A      S H E E T

## SUBJECT:

Technical Report entitled "Synthesis of Energetic Oxidizers by Radiation Techniques", S-14110, by R. M. Curtis, and J. N. Wilson, generated by the Shell Development Company under Contract F04611-69-C-0074, Project No. 3148.

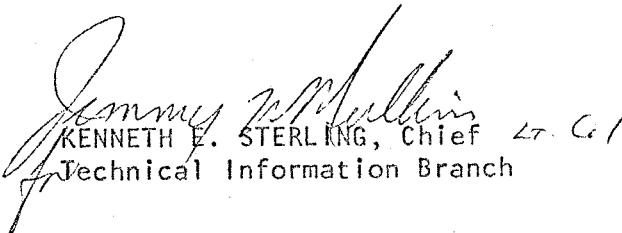
Final Technical Report - April 1969 - December 1970.

## ACTION:

Add as Technical Report Number - AFRPL-71-105.

Delete Distribution Statement on Front Cover and also on Page 14, Item 10 of DD Form 1473 (last page of report).

Substitute Distribution Statement: "Approved for public release; distribution unlimited" in both of above referenced locations.

  
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SYNTHESIS OF ENERGETIC OXIDIZERS  
BY RADIATION TECHNIQUES

Sponsoring Agency: Air Force Rocket Propulsion Laboratory  
Research and Technology Division  
Air Force Systems Command, USAF

Contract No. FO4611-69-C-0074  
AFFTC Project No. 3148  
BPSN 623148

FINAL TECHNICAL REPORT

April 1969-December 1970

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August 1971

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Shell Development Company  
A Division of Shell Oil Company  
Emeryville, California

## FOREWORD

The work described in this report was authorized under AFFTC Project No. 3148, BPSN 623148. The contract project officer was initially Dr. F. Q. Roberto and later Dr. Robert Merrill, Air Force Rocket Propulsion Laboratory, RPCS, Edwards, California.

This Final Technical Report on Contract No. F04611-69-C-0074 describes the work carried out by Shell Development Company, Emeryville, California during the period 1 April 1969 to 31 December 1970 on the application of energetic radiation to the attempted synthesis of several specified potential high energy oxidizers. None of the compounds sought were successfully prepared.

This report has been reviewed and is approved.

# ABSTRACT

Ionizing radiation at liquid nitrogen temperature was employed in an attempt to synthesize some previously unknown energetic oxidizers whose possible existence was postulated.

The specific compounds sought were  $\text{ClF}_7$ ,  $\text{BrF}_7$ ,  $\text{ClF}_5\text{O}$  and a polymer of  $\text{N}_2\text{F}_2$ .

None of the compounds sought were successfully isolated or identified from the reaction mixtures tested. The methods used in this investigation are described.

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DOCUMENT CONTROL DATA - R AND D; DD Form 1473 with Abstract and  
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## SYNTHESIS OF ENERGETIC OXIDIZERS BY RADIATION TECHNIQUES

### OBJECTIVES AND SUMMARY OF RESULTS

This contract was undertaken with the following specific objectives: the synthesis of  $\text{ClF}_7$ ,  $\text{BrF}_7$  and  $\text{ClF}_5\text{O}$  and the polymerization of  $\text{N}_2\text{F}_2$  using radiation chemistry techniques. The general approach in this effort has involved exposure of appropriate reagents at low temperature to bremsstrahlung from a 3 Mev Van de Graaff generator and subsequent analysis by various techniques for indications of new products. No direct evidence indicating formation of any of the entities mentioned above has been found. If such products were formed under the conditions used herein, their concentrations were too small for detection by the methods used by us and/or they were too unstable to survive even gentle attempts at their isolation.

During the course of this work chronic difficulties were encountered with contamination of the vacuum system and with leaks, both resulting from the highly corrosive nature of the compounds under investigation. These effects resulted in the formation of by-products which complicated the interpretation of the observations and increased the difficulty of detecting small amounts of the compounds being sought.

### APPARATUS

Work under this contract was started with a pre-existing vacuum system. Because of rigid construction this system proved very difficult to clean and to modify by adding or removing traps and fittings as needed for particular experiments. An alternative demountable vacuum system was therefore constructed that has proved to be very satisfactory. Our experience with this system has generally been good and a few observations that may be of interest for future work are reported here.

The demountable vacuum system was constructed from 3/8" stainless steel tubing, Cajon precision pipe fittings and Cajon VCR ultra high vacuum couplings. Hoke diaphragm seal valves in tee and straight patterns using Kel-F seals and stem points were used. This vacuum system incorporated two thermocouple gages, a Heise gage (0-800 mm, stainless steel bourdon tube), two mechanical forepumps and a mercury diffusion pump. The diffusion pump was protected by two liquid nitrogen traps in series with provision that the first trap, connected to the main section of the vacuum system, could be isolated, raised to room temperature, and pumped out separately through a forepump which also served as a roughing vacuum for the entire system. In addition to operating on fluorocarbon pump oil this roughing pump was protected by a carbon trap kept at 500°C and a soda lime trap. We have found that forepumps can operate continuously for over a year on fluorocarbon oil without trouble. However, this oil shows a marked drop in viscosity at operating temperature and, unless the pump has a good seal and a very smooth shaft, leakage can be a problem after a very short operating period.

The operating portion of this vacuum system includes the Heise gage, one thermocouple gage for low pressure readings, provision for connecting up to four sample vessels or gas cylinders, and direct connections to nitrogen gas for purging and fluorine gas for experiments. The volume is about 100 cm<sup>3</sup> and in addition a one liter storage tank can be opened to the system for handling larger

gas volumes. Typically the system (100 cm<sup>3</sup>) is pressured to a few hundred torr with the desired reagent vapor which is then condensed with liquid nitrogen for later irradiation into a 1/4" diameter reactor tube of either stainless steel or sapphire. A second reagent, if required, is similarly condensed and finally when fluorine is to be used it is condensed last since its 300 mm vapor pressure at liquid nitrogen temperature prevents any further condensation of other reagents. With fluorine present it is necessary to stay at or very close to liquid nitrogen temperature where most other reactants are solids. This presents difficulties so far as efficient mixing of reactants prior to irradiation and three methods were tried to improve this mixing. One approach, the most often used, involved condensing the solidifying phases into a precooled reactor tube. In this way the walls are coated with solid and with excess fluorine present one is assured of at least a fairly extensive liquid-solid interfacial area. A relatively unsuccessful approach was to condense while a vibrator was attached to the reactor tube, the hope being to obtain a more or less powdered condensate. The most novel approach reversed the above sequence in that fluorine was condensed initially after which the phase to be solidified was rapidly introduced at a pressure well above that of fluorine. The result was a small amount of condensation in the liquid fluorine as a fairly fine powder but an inability to transfer very much material in this way.

As described later, fluorine can be purified by an irradiation technique and it proved desirable to have a supply of such purified fluorine available in addition to the supply directly from a cylinder. Purified fluorine was stored in a 50 cm<sup>3</sup> stainless steel cylinder attached by a relatively long section of tubing to the vacuum system. The tubing was arranged so that the cylinder could be kept inside a ten liter liquid nitrogen dewar with holding time of better than two weeks. By lowering the dewar on a lab jack the cylinder could be gradually warmed to give whatever fluorine pressure was desired.

As mentioned earlier, the valve stems in the vacuum system were Kel-F. These stems are pressed into seats which in turn are silver soldered to stainless steel diaphragms. Difficulty was experienced with attack of the silver solder by reagents in the system and on several occasions valves had to be replaced when leaks developed. Kel-F itself is not completely inert. For example, cracking occurred in contact with O<sub>2</sub>F<sub>2</sub>. A few valves were altered by replacing the Kel-F stems with gold. While this proved satisfactory, the difficulties noted produced only occasional inconvenience and were not so serious as to require the installation of the altered valves. One shipment of valve stems as received contained both stems of Kel-F and what was probably polyethylene or polypropylene. Although these can be distinguished visually the difference is not great and was not realized prior to installation. Needless to say the first contact with oxidizing reagents led to a vigorous reaction with stems not made of Kel-F.

Only one small explosion occurred during this work. In cleaning reactor tubes our procedure had been to give a final rinse with acetone prior to drying. Apparently some of this acetone remained after attachment to the vacuum system and was caught in a steel U tube trap containing ClF<sub>3</sub>. During later warming this trap ruptured but without damage beyond rendering the trap useless.

Irradiations were performed<sup>1)2)</sup> by placing reactor tubes in a stainless steel dewar arranged with automatic filling of liquid nitrogen. The electron beam

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1) See Bibliography.

from a 3 Mev Van de Graaff generator is deflected to a horizontal plane and strikes a gold target. Bremstrahlung from this target then penetrates the dewar and sample. Dose rate at the sample is about 100 megarads per hour. Exposure times between 1/2 and 3 hours were used, depending on the particular experiment.

## INSTRUMENTATION

Our primary analytical tool in this work was a Quad 200 quadrupole mass spectrometer (Electronic Associates, Inc., Palo Alto, California). In this instrument as originally received, the mass analyzer and associated ionization chamber were cantilevered coaxially from a heavy base plate that formed one end of a horizontal stainless steel cylinder, six inches in diameter; gas samples to be analyzed were introduced through a hole in the base plate at the other end. Since the distance from this hole to the ionization chamber was substantial, entering gas molecules had many opportunities to collide with the walls before entering the ionization region. In this configuration the sensitivity of the instrument to reactive gases such as  $F_2$  or  $ClF_3$  was very low and not very reproducible. During the course of this work both the sensitivity and reproducibility were improved by changing the sample introduction system to a coaxial tube that was led through the base plate and terminated a short distance from the entrance to the open ionization chamber at which it was aimed. With this arrangement, incoming gases were much more likely to enter the ionization chamber before colliding with the walls.

The walls of the cylinder housing the mass analyzer were equipped with heating coils which had proved useful in minimizing contamination of the quadrupole rods when the instrument was used to analyze organic compounds. In the present work, use of the heating coils had a deleterious effect in accelerating corrosive attack on the quadrupole rods by the highly oxidizing materials under investigation. The resulting insulating deposits on the rods give rise to stray electric fields that cause erratic operation and a loss of resolution. Such effects were troublesome in the early phases of this work until the source of the difficulty was recognized, the heating coils were disconnected and the rods were carefully cleaned.

A roughly calibrated variable leak between the sample handling system and the inlet to the mass spectrometer was used to estimate the pressure of the incoming sample. Reactor tubes containing samples were attached through a system of valves, traps and pump to the inlet. Schematic diagrams of both the demountable vacuum system and the mass-spectrometer inlet system are shown in Figure 1.

In operation, a reactor tube is attached while at liquid nitrogen temperature and is then raised through a set of temperatures fixed by immersion in slush baths. A typical sequence is  $-196^\circ$  (liquid  $N_2$ ),  $-160^\circ$  (isopentane),  $-130^\circ$  (n-pentane),  $-95^\circ$  (toluene),  $-75^\circ$  (dry ice/acetone),  $-24^\circ$  ( $CCl_4$ ) and room temperature. At each temperature step the sample may be pumped to remove volatiles, with pressure noted on a thermocouple gage, and vapor may be introduced to the mass spectrometer. Unfortunately the inlet system to the spectrometer is at room temperature and while this is substantially less than the temperature of ionization it is still high enough for possible decomposition of low temperature volatiles before they reach the spectrometer inlet.

Infrared analyses were carried out using a low temperature cell with the product between AgCl plates held in a brass block cooled by liquid nitrogen, a surrounding vacuum, and CsBr windows between the vacuum and external atmosphere.

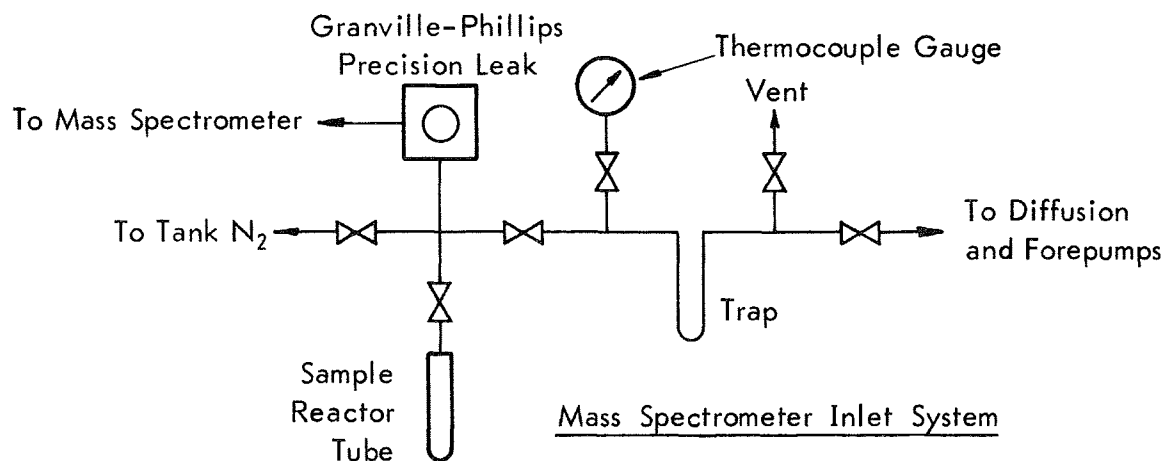
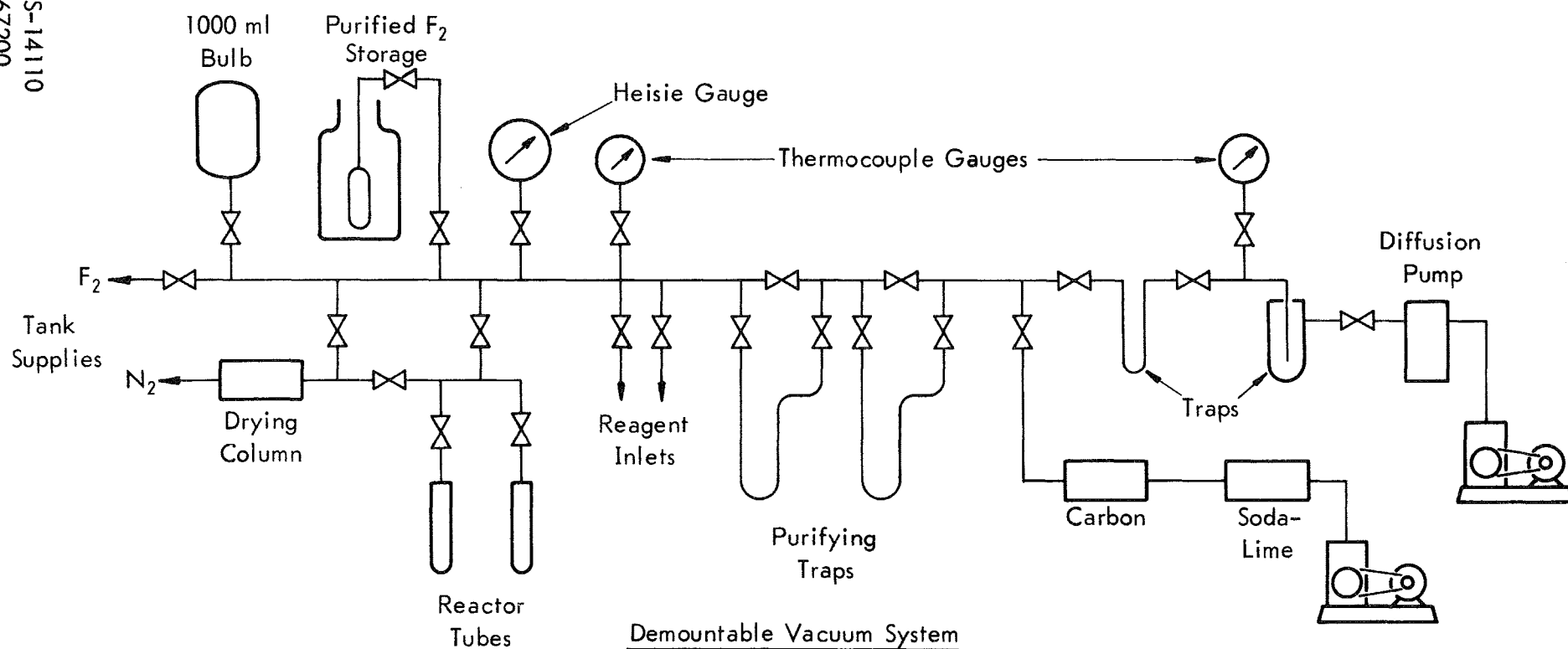


Figure 1. VACUUM SYSTEMS

For a description, see Reference 3. Transfer of sample from a reactor tube to the precooled AgCl plates is carried out in a nitrogen atmosphere (dry box). This procedure has worked rather well with a number of samples but is amenable to improvement on two points. During transfer it is possible for the sample temperature to rise above liquid nitrogen temperature and it is also difficult to maintain a completely dry atmosphere. These factors could result in the decomposition of a very unstable species prior to its infrared analysis.

For Raman spectroscopy use was made of a 1/8" diameter sapphire reactor tube cooled by cold nitrogen gas. The reactor tube was inserted in an insulating styrofoam block with holes at right angles for the incident laser beam and scattered beam. To avoid condensation on the reactor tube prior to insertion in the foam block, a tight fitting plastic straw was slipped over the tube and removed once it was in place. With this arrangement samples could be irradiated and Raman spectra run without transfer or exposure to an external atmosphere. Temperatures down to about  $-120^{\circ}$  could be maintained. Some spectra were obtained with an alternative cell in which the sample was held in a small slot in the face of a copper block cooled by liquid nitrogen. The block face was cut at  $45^{\circ}$  from vertical such that a laser beam entering from above was scattered in a horizontal plane. Experience showed that this cell was effective in principle but that an o-ring seal used to close the vacuum jacket and attach an exit window required extensive re-design since minor leaks through it allowed traces of water vapor to enter the jacket and react with the sample. This not only changed the composition of the sample but also gave rise to serious corrosion problems. Since this cell was developed rather late in the project, the decision was made not to attack the problem of re-design but to use the simpler system described above for the Raman work.

#### EXPERIMENTAL PROBLEMS

As indicated earlier a major tool in this work has been mass spectrometry. One of the discoveries with this tool has been the almost ubiquitous presence of oxygen in experimental preparations that were supposedly oxygen free. The sources of this oxygen were varied and it was not until near the final phases of this work that the oxygen level could be reduced, when necessary, to an amount where it would not play a significant role in the results. Three particular sources of oxygen were distinguished; incomplete system passivation, valve leaks caused by reactions with valve components in the sample-handling system, and leaks through the reactor tube closure valve during irradiation or at the sapphire to metal seal. System passivation, as ultimately applied, involved steam cleaning followed by contact with  $\text{ClF}_3$  for an extended (48 hours) time. Occasional steam cleaning was necessary to remove accumulated deposits, particularly in the valves;  $\text{ClF}_3$  was used for passivation because of its reactivity and ready availability and it proved particularly satisfactory prior to work with  $\text{ClF}_5$  and  $\text{NF}_3$ . Passivation was considered adequate when the mass spectrum of  $\text{ClF}_3$ , held in the system for some hours, revealed none of the oxides  $\text{ClO}^+$ ,  $\text{ClO}_2^+$ ,  $\text{ClO}_3^+$  and  $\text{ClO}_3\text{F}^+$ . Valve leaks were somewhat difficult to detect because of the spring loading on the diaphragm. Thus a valve might slowly leak at one setting but not at another. On three occasions sapphire reactor tubes developed leaks that required return to the manufacturer for repair. These leaks always occurred at the soldered joint between the end of the sapphire section and the stainless steel (later changed to nickel) upper section and doubtless arose from thermal stress when the sapphire tube was cooled. These leaks occurred only during warming or cooling and were not evident at room temperature. One other source of oxygen was the approximately 1/2%

present in the fluorine supply. Purification involved 1/2 hour irradiation followed by distillation of the fluorine at liquid oxygen temperature ( $-183^{\circ}\text{C}$ ) to a container at  $-196^{\circ}\text{C}$ . The oxygen fluorides formed are left behind as a solid. Repetition of the operation purified the fluorine to an oxygen content substantially under 0.1%.

An additional problem in the mass spectrometry of interhalogen compounds arises through abstraction of fluorine from the sample compound by reaction with the walls. When the vapor pressure over the sample is low, and that was often the case in the work reported here, the molecules in the vapor space between the sample and the variable leak suffer a great many collisions with the walls during their residence time in that space. Passage through the variable leak involves a great many collisions with metal surfaces also. Unless passivation is virtually complete, some of these collisions will lead to fluorine abstraction from halogen fluorides. Thus our mass spectra of ClF always contained a substantial  $\text{Cl}_2^+$  peak as well as the expected  $\text{ClF}^+$ , even after attempted purification. In the early phase of the program, before severe passivation techniques were adopted, the intensity ratio  $\text{Cl}_2^+/\text{ClF}^+$  was of order of magnitude unity. In one experiment a sample of ClF gas in a sapphire reaction vessel at room temperature and a few hundred torr displayed an initial mass spectrum in which the intensity ratio  $\text{Cl}_2^+/\text{ClF}^+$  was 0.5; significant peaks were observed also for  $\text{ClO}^+$  and  $\text{ClO}_2^+$ . About half of the gas was contained in the reaction vessel and about half in the transfer line. After one hour of standing at room temperature the mass spectrum was measured again; all trace of  $\text{ClF}^+$  had disappeared. Note that ClF is thermodynamically stable relative to  $\text{F}_2$  and  $\text{Cl}_2$  under these conditions.

As an additional example, after redesign of the inlet to the mass spectrometer but before the development of the more intensive passivation procedures, the mass spectrum of  $\text{ClF}_5$  was in reasonable agreement with that of Pilipovich et al<sup>4)</sup> in regard to the relative intensities of  $\text{ClF}_4^+$ ,  $\text{ClF}_3^+$  and  $\text{ClF}_2^+$  but the intensity of  $\text{ClF}^+$  was too high by a factor 4 and that of  $\text{Cl}_2^+$  was nearly half that of  $\text{ClF}_2^+$ .

Under these circumstances, only qualitative reliance could be placed on the mass spectra unless reference spectra were taken at nearly the same time and under similar conditions. For these reasons, in the later stages of the program, increased reliance was placed on other spectroscopic techniques. Unfortunately,  $\text{F}^{19}$  NMR was not available to us on a routine basis.

#### EXPERIMENTAL RESULTS WITH VARIOUS REAGENTS

In the paragraphs below we describe the experimental work on the basis of the principal reactant. Irradiation experiments were carried out generally as described earlier and the reactions thus induced were inferred from observations of the mass spectra at a series of increasing temperatures supplemented by some infrared analyses. The general problem of oxygen in supposedly oxygen free systems has been noted. Features peculiar to individual experiments are noted below where appropriate.

##### ClF

Only one irradiation was carried out on ClF. The vapors released up to  $-75^{\circ}\text{C}$  gave mass spectral peaks corresponding to  $\text{ClF}^+$ ,  $\text{F}_2^+$  and  $\text{Cl}_2^+$  together with impurity peaks of uncertain origin corresponding to  $\text{O}_2^+$ ,  $\text{ClO}^+$  and  $\text{ClO}_2^+$ . After the sample vessel had been held for one hour at  $-75^{\circ}\text{C}$  (note ClF boils at  $-100^{\circ}\text{C}$ )

but with the transfer line at room temperature, mass spectral peaks for  $\text{ClF}_2^+$  and  $\text{ClF}_3^+$  were observed. These presumably arose from  $\text{ClF}_3$  formed by reaction between  $\text{ClF}$  and  $\text{F}_2$  at room temperature. Thus the primary radiation induced process in  $\text{ClF}$  is decomposition to the elements.

### $\text{ClF}_3$

Mass spectra at room temperature of unirradiated  $\text{ClF}_3$  were run at various times throughout this project, largely to check passivation. The best examples, those showing no evidence of oxides, averaged the following relative peak intensities:  $\text{Cl}^+(33)$ ,  $\text{F}^+(0.1)$ ,  $\text{Cl}_2^+(18)$ ,  $\text{ClF}^+(100)$ ,  $\text{ClF}_2^+(99)$ ,  $\text{ClF}_3^+(3)$ . Other samples revealed varying degrees of decomposition characterized by decreasing relative intensity for  $\text{ClF}^+$ ,  $\text{ClF}_2^+$  and  $\text{ClF}_3^+$  and increasing intensity of  $\text{Cl}_2^+$  and the possible oxides,  $\text{ClO}^+$ ,  $\text{ClO}_2^+$ ,  $\text{ClO}_3^+$ ,  $\text{ClO}_4^+$  and  $\text{ClO}_3\text{F}^+$ . Three low temperature irradiations carried out with and without excess fluorine present each produced  $\text{ClF}_5$  as evidenced by a  $\text{ClF}_4^+$  peak. The significant peaks in this case at  $-75^\circ$  (the maximum for  $\text{ClF}_4^+$ ) had relative values of  $\text{ClF}^+(100)$ ,  $\text{ClF}_2^+(10)$ ,  $\text{ClF}_3^+(2)$  and  $\text{ClF}_4^+(10)$ . The relatively low intensity for  $\text{ClF}_2^+$  here compared to that with unirradiated  $\text{ClF}_3$  may be noticed but it is difficult to draw any significant conclusions concerning kinetics under these experimental conditions.

### $\text{ClF}_5$

One of the major hopes of this work was that the reaction  $\text{ClF}_5 + \text{F}_2 = \text{ClF}_7$  would occur under irradiation. Eleven irradiation experiments were performed with ratios of  $\text{F}_2/\text{ClF}_5$  ranging from 0/1 to 10/1. A number of these experiments were contaminated with oxygen but in a few cases the oxygen level was sufficiently low that it could not influence the results, this being inferred from the absence or near absence of peaks corresponding to  $\text{O}_2^+$ ,  $\text{OCl}^+$ ,  $\text{ClO}_2^+$  etc.

Since the melting point of  $\text{ClF}_5$  ( $-103^\circ\text{C}$ )<sup>4</sup> is much higher than the irradiation temperature of  $-196^\circ\text{C}$ , it was desirable to disperse the  $\text{ClF}_5$  as well as possible in the liquid  $\text{F}_2$ . The following method was devised to accomplish this: liquid fluorine is condensed in one leg of an inverted u-tube at  $77^\circ\text{K}$  and  $\text{ClF}_5$  in the other. The valves isolating the two legs from each other are then opened and the leg containing  $\text{ClF}_5$  is warmed rapidly to  $0^\circ\text{C}$  by immersion in ice water. The resulting rapid distillation of the  $\text{ClF}_5$  into the liquid  $\text{F}_2$  results in a fine dispersion of the  $\text{ClF}_5$ , especially if the volume ratio of  $\text{F}_2/\text{ClF}_5$  is appreciably greater than unity.

With a well passivated system, the relative intensities in the mass spectrum of unirradiated  $\text{ClF}_5$  were found to correspond to  $\text{ClF}_4^+(100)$ ,  $\text{ClF}_3^+(20)$ ,  $\text{ClF}_2^+(100)$ ,  $\text{ClF}^+(40)$ . The intensity of  $\text{ClF}^+$  depends on the quality of passivation. Considering the difference in apparatus, conditions and type of mass spectrometer, this result is in reasonable agreement with that of Pilipovich et al<sup>4</sup>) with a CEC 21-103 mass spectrometer:  $\text{ClF}_4^+(82)$ ,  $\text{ClF}_3^+(18.6)$ ,  $\text{ClF}_2^+(100)$ ,  $\text{ClF}^+(21.0)$ .

Pilipovich et al did not report seeing the parent ion,  $\text{ClF}_5^+$ , and we have not detected it in most of our spectra. We did observe a very faint doublet at masses 130-132, corresponding to  $\text{ClF}_5^+$ , in two instances, however. The relative intensity on the above scale was 0.2 in both cases. One instance was in the spectrum of unirradiated  $\text{ClF}_5$  and the other was in the spectrum of the products of an irradiation experiment with  $\text{F}_2/\text{ClF}_5$ . We believe that the  $\text{ClF}_5^+$  ion observed is the true parent ion and does not provide convincing evidence for the existence of

a higher fluoride than  $\text{ClF}_5$ . Similar observations were made with  $\text{BrF}_5$  (vide infra).

An interesting observation in this group of irradiation experiments was the delayed release of fluorine as indicated by the  $\text{F}_2^+$  peak. Whereas fluorine should be observed at  $-196^\circ\text{C}$  and pumped off at this temperature, it was frequently found throughout a warming cycle to as high as  $-75^\circ\text{C}$  despite pumping at lower temperatures. Our initial interpretation of this was that an unstable fluorine compound was formed which decomposed on warming with the release of elemental fluorine. Such a compound could be the desired  $\text{ClF}_7$  but the presence of oxygen rendered such a conclusion tentative. Although later "clean" (oxygen free) runs continued to show this effect, it was noticed that the peak release of fluorine occurred near the melting point of  $\text{ClF}_5$ . This prompted an alternative explanation, which seems more likely, that irradiation of solid  $\text{ClF}_5$  results in some decomposition (to  $\text{ClF}_3 + \text{F}_2$  for example) with the fluorine trapped in the crystalline lattice. Upon warming there is some release by diffusion of fluorine up to the melting point when the remainder is released. Reexamination of the  $\text{ClF}_3$  data revealed a similar result so far as fluorine release and here since only a minute amount of  $\text{ClF}_5$  was present, the chance of forming a higher fluoride than  $\text{ClF}_5$  is quite remote.

Infrared spectra were run at liquid nitrogen temperature on a number of samples of  $\text{ClF}_5$  itself and on samples that had been subjected to radiation both with and without the addition of fluorine. No new absorption bands were detected in the irradiated samples. In  $\text{ClF}_5$  vapor<sup>5)</sup> major infrared bands occur at 486, 541, 732 and  $786\text{ cm}^{-1}$ . In solid  $\text{ClF}_5$ <sup>6)</sup> the band at  $486\text{ cm}^{-1}$  shows isotopic splitting ( $483, 493\text{ cm}^{-1}$ ), those at 541 and  $786\text{ cm}^{-1}$  are unchanged, and the intense band at  $732\text{ cm}^{-1}$  is shifted to  $680\text{ cm}^{-1}$ . In addition, what are presumably lattice modes appear at 725 and  $743\text{ cm}^{-1}$ . Collectively, among the various  $\text{ClF}_5$  specimens examined, we have observed all the bands reported by Christie<sup>6)</sup> for the solid. The doublet at 483 and  $493\text{ cm}^{-1}$  was almost always resolved and appears to be the most distinctive identifying feature. In the  $650\text{--}800\text{ cm}^{-1}$  region often only a single broad band appeared. At least in part, this was due to the experimental complexities which permitted only a single infrared sample preparation from a given experiment. Absorption in this region occurs also with  $\text{ClF}_3$  and  $\text{ClOF}_3$ . One instance of bands not due to  $\text{ClF}_5$  was observed with unirradiated  $\text{ClF}_5$ . These extraneous bands were doubtless due to impurities and were not observed in other similar samples.

In general, the infrared spectra of the  $\text{ClF}_5$  reaction samples gave evidence for the presence of  $\text{ClF}_5$  only. This provides another reason for believing that many of the complexities of the mass spectra observed for vapors from these samples were due to wall reactions.

A great deal more fine structure is discernible in the infrared spectrum of the vapor of  $\text{ClF}_5$  than in that of the solid; it is likely that the spectrum of liquid  $\text{ClF}_5$  will show an intermediate amount of detail. If further work of this kind is done, it may be useful to record infrared spectra just above the melting point of the solid, in the region  $-95$  to  $-100^\circ\text{C}$ , in order to increase the diagnostic utility of the spectra.

Two low temperature raman spectra were obtained, one on  $\text{ClF}_5$  and one on an irradiated mixture of  $\text{ClF}_5 + \text{F}_2$ . In both cases a single peak at  $480\text{ cm}^{-1}$  was observed, consistent with the infrared conclusion that only  $\text{ClF}_5$  was being detected. Our Raman spectroscopy technique did not reach a state of perfection such as to



provide more detailed information but in view of the infrared and mass spectrometric results on  $\text{ClF}_5$ , it seems rather definite that  $\text{ClF}_7$  was not produced in significant amounts.

### $\text{BrF}_5$

Because  $\text{IF}_7$  exists it seems much more likely that the heptafluoride of bromine could be prepared than that of chlorine. Some early experiments involving irradiation of mixtures of fluorine with compounds purported to be  $\text{BrF}_3$  and  $\text{BrF}_5$  came to no conclusions when it was found that the reagents were essentially only  $\text{Br}_2$  and contained little of the expected bromofluorides. A suitable sample of  $\text{BrF}_5$  was finally secured and two irradiation experiments were carried out involving  $\text{BrF}_5 + \text{F}_2$  following the same techniques used with  $\text{ClF}_5$ . Infrared measurements were not made but a very careful search by mass spectrometer was made for fluoride species higher than the principal ion  $\text{BrF}_4^+$ . Only an extremely weak doublet corresponding to the parent,  $\text{BrF}_5^+$ , was found. This occurred in both the irradiated samples of  $\text{BrF}_5 + \text{F}_2$  and in unirradiated  $\text{BrF}_5$ . Consistent with the work on  $\text{ClF}_5$ , a peak intensity for  $\text{F}_2^+$  was observed near the melting point of  $\text{BrF}_5$ . Thus it seems that the behavior of  $\text{BrF}_5$  is analogous to that of  $\text{ClF}_5$  under radiation and like  $\text{ClF}_5$  gives no indication of higher fluoride formation. With our instrument the relative intensities in the mass spectrum of  $\text{BrF}_5$  are  $\text{BrF}_5^+$ , 0.1;  $\text{BrF}_4^+$ , 100;  $\text{BrF}_3^+$ , 30;  $\text{BrF}_2^+$ , 50 and  $\text{BrF}^+$ , 30.

### $\text{OClF}_3$

During work with  $\text{ClF}_3$  and  $\text{ClF}_5$  we did not observe the formation of  $\text{OClF}_3$  despite the frequent presence of some oxygen. Since fluorox is relatively stable one might expect its occurrence in some of the above experiments. On the other hand, its absence says nothing about its own radiation chemistry and thus the reaction  $\text{OClF}_3 + \text{F}_2 = \text{OClF}_5$  was considered a possibility. Only one irradiation of  $\text{OClF}_3 + \text{F}_2$  at  $-196^\circ\text{C}$  was performed and neither mass spectrometry nor infrared analysis indicated any novel products.

### $\text{NF}_3$

The system  $\text{NF}_3 + \text{ClF}_5$  offers the possibility of forming  $\text{NF}_4^+\text{ClF}_4^-$  and accordingly was looked at in some detail. Five irradiation experiments included  $\text{NF}_3$  alone,  $\text{NF}_3 + \text{ClF}_5$ , and  $\text{NF}_3 + \text{ClF}_5 + \text{F}_2$ . No unexpected products were observed either by mass spectrometry or by low temperature infrared analysis. The one interesting observation concerns the release of  $\text{N}_2$  and  $\text{F}_2$ , as detected by  $\text{N}_2^+$  and  $\text{F}_2^+$  peaks mass spectrometrically. As indicated earlier  $\text{ClF}_5$  under irradiation forms some fluorine which is only finally released near the melting point of  $\text{ClF}_5$ . In a single irradiation experiment on neat  $\text{NF}_3$  we observed nitrogen, as expected, but only a small amount of fluorine at  $-196^\circ\text{C}$ . Since  $\text{NF}_3$  is a liquid at this temperature trapping of  $\text{F}_2$  is not possible and consistent with this no nitrogen or fluorine was observed above  $-196^\circ\text{C}$ . However, irradiation of mixtures ( $\text{ClF}_5 + \text{NF}_3$ ) always resulted in some  $\text{F}_2^+$  at  $-196^\circ\text{C}$ , negligible  $\text{F}_2^+$  at  $-130^\circ$  (after pumping at a lower temperature) followed by a definite  $\text{F}_2^+$  peak when warmed to  $-95^\circ\text{C}$ . This behavior is similar to that observed with  $\text{ClF}_5$  alone. An inadvertent confirmation of the trapping of  $\text{F}_2$  in  $\text{ClF}_5$  came about on one occasion as follows. Two irradiated samples of  $\text{ClF}_5 + \text{NF}_3$  were stored overnight prior to mass spectrometer runs. They were stored in a dewar with liquid nitrogen and in order to retain the liquid nitrogen longer the dewar and samples were placed in a dry ice chest. By the next day the nitrogen had evaporated and the samples presumably had warmed to

-75°C. Despite this mass spectrometer runs were made in the usual way starting at -196° with stepwise warming. In both cases a strong  $F_2^+$  peak was observed at liquid nitrogen temperature and after pumping no further fluorine was detected at higher temperatures. This is readily accounted for by the hypothesis of fluorine generation in the  $ClF_5$  lattice and release upon melting.

### $N_2F_2$

One of the original objectives under this contract was the search for a possible polymerization of  $N_2F_2$ . Difluorodiazene was prepared, following Johnson<sup>6</sup>) by the reaction of 5N base on 1N aqueous N,N-difluorourea. No attempt was made to separately prepare the cis and trans isomers. The product as used was mainly the trans isomer but included about 10%  $N_2F_4$ . A group of irradiation experiments with and without possible metallic catalysts failed to give any solid product (at -75°) or mass spectra revealing any unexpected products. While in one instance a solid was isolated, it was found to contain oxygen and to occur only when oxygen was present. This product was not characterized beyond determining its melting point (-28°C) and mass spectrum ( $M/E = 30, 44$  and  $47$ ).

A series of irradiation experiments were carried out on this material in a variety of reaction vessels. Earlier exploratory work had indicated that the polymerization reaction might be catalyzed by unpassivated metals. Thus, irradiations were done in sapphire, in unpassivated stainless steel and in a sapphire tube containing stainless steel mesh. In all cases mass spectrometric examination of volatiles from the irradiated samples revealed only  $N_2$ ,  $F_2$ ,  $NF_3$  and unreacted  $N_2F_2$ .

A solid product (white powder) was recovered from one experimental irradiation of an equimolar mixture of  $N_2F_2$  and  $F_2$  in a sapphire tube containing a short length of stainless steel tubing. The solid was found to decompose at -28°C to yield vapors whose mass spectrum contained major peaks at mass 47 ( $N_2F^+$ ), 44 ( $N_2O^+$  or  $CO^+_2$ ) and 30 ( $NO^+$ ). Thus the solid apparently contained oxygen. The amount of solid recovered was too small for additional characterization. An examination of the starting materials showed that the purified fluorine had become contaminated with oxygen. A repeat irradiation experiment with  $N_2F_2$  and freshly purified  $F_2$  gave no products solid at -78°C. A white solid product could be produced, however, by spiking the same reaction mixture with oxygen prior to irradiation. Since  $O_2$  is readily converted to  $O_2F_2$  under the conditions of these experiments, the recovered powder may be a product of a reaction between  $O_2F_2$  and  $N_2F_2$ . Since our major interest was in the homopolymer of  $N_2F_2$  and since the thermal stability of the product was low, the nature of the solid or of the reaction leading to it was not investigated further. A more detailed study of this system may well be of academic interest.

### $O_2F_2$

Some work was carried out with  $O_2F_2$  based on its properties as a strong fluorinating agent rather than on radiation chemistry. It was conjectured that  $O_2F_2$  might convert  $ClF_5$  or  $BrF_5$  to the corresponding heptafluoride. Equimolar mixtures of  $O_2F_2$  with  $ClF_3$ ,  $ClF_5$ ,  $OClF_3$ ,  $BrF_5$  and  $ClF_5$  plus  $F_2$  were kept at -75°C for times extending up to one week. In all cases decomposition of the  $O_2F_2$  occurred and in two cases, with  $ClF_3$  and  $OClF_3$ , a nearly quantitative yield of  $ClF_5$  resulted. Apart from this no new products of significance were observed. In the two cases where  $ClF_5$  was formed fluorine from  $O_2F_2$  was consumed and the only

other product was  $O_2$ . In the other cases the decomposition of  $O_2F_2$  resulted in an equimolar mixture of  $O_2$  and  $F_2$ .

### CONCLUSIONS

As noted in the introduction, we have been unable to demonstrate production of any of the entities that were the objectives of this project. The techniques for detecting such possible products could be improved over those noted above. For example, the mass spectrometer inlet system could be precooled and perhaps should be internally plated with silver or gold. Improved techniques for infrared and Raman analysis could be developed and it would be useful also to make use of  $F^{19}$  NMR. Improvements in chemical techniques are also possible. The feasibility of a low temperature solvent such as  $CF_4$ ,  $NF_3$  or  $F_2$  for carrying out irradiations in the liquid phase was considered but not explored. A suitable solvent at liquid nitrogen temperature might, however, be difficult to find since we observed only negligible solubility of chlorine fluorides in  $F_2$  and of  $ClF_5$  in  $NF_3$ . While such improvements are feasible and might lead to a better understanding of those chemical changes which were observed it does not seem likely that they would lead to observation of the species sought under this contract.

A table summarizing the experiments performed under this contract is appended.

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Table 1. INFRARED ANALYSES

Composition (Mole Ratios)			Irradiations		Observed Frequencies (cm <sup>-1</sup> )									
ClF <sub>5</sub>	F <sub>2</sub>	Other	(megarads)											
1	XS	O <sub>2</sub> F <sub>2</sub> , 1	none	370*	457*	482	495	611*	700bd		785			
1	9	--	125			482	495		700bd		785	840		
1	2.5	--	70			482	496		720bd					
1	3	--	300			488bd			730bd			845		
1	--	NF <sub>3</sub> , 1.7	200			481	494		715bd					
1	--	NF <sub>3</sub> , 1.7	200			480	493	540	685	720	745	783		
1	(Literature) <sup>e</sup>		none	385		482	493	539	681	725	743	780	841	

\*O<sub>2</sub>F<sub>2</sub> bands.

Table 2. MASS SPECTROMETER RESULTS

Sample Composition	Milli- moles	Irradiation megarads	Strongest Peaks After Warming to Selected Temperatures*			
			-160°C	-130°C	-75°C	-20°C
ClF	neat	150		Cl <sub>2</sub> , ClF	ClF, Cl <sub>2</sub>	
ClF <sub>3</sub>	neat	75		ClF, Cl <sub>2</sub>	ClF, Cl <sub>2</sub>	ClF <sub>2</sub> , ClF
ClF <sub>3</sub> /F <sub>2</sub>	0.6/1.1	100		O <sub>2</sub> , F <sub>2</sub>	ClF, F <sub>2</sub>	ClF <sub>2</sub> , ClF
ClF <sub>3</sub> /F <sub>2</sub>	3.0/6.0	75	F <sub>2</sub> , ClF	ClF, O <sub>2</sub>	ClF, Cl <sub>2</sub>	ClF, ClF <sub>2</sub>
ClF <sub>5</sub>	neat	150		F <sub>2</sub> , O <sub>2</sub>	Cl <sub>2</sub> , O <sub>2</sub>	Cl <sub>2</sub> , ClO <sub>2</sub>
ClF <sub>5</sub>	neat	50		O <sub>2</sub> , F <sub>2</sub>		Cl <sub>2</sub> , ClO <sub>3</sub>
ClF <sub>5</sub> /F <sub>2</sub>	3.0/6.0	50		F <sub>2</sub> , Cl <sub>2</sub>	F <sub>2</sub> , Cl <sub>2</sub>	ClF <sub>2</sub> , ClF
ClF <sub>5</sub> /F <sub>2</sub>	3.0/6.0	50		F <sub>2</sub> , ClF <sub>4</sub>	ClF <sub>4</sub> , F <sub>2</sub>	
ClF <sub>5</sub> /F <sub>2</sub>	1.0/2.0	50	CF <sub>3</sub> , F <sub>2</sub>	F <sub>2</sub> , Cl <sub>2</sub>	F <sub>2</sub> , ClF <sub>4</sub>	CF <sub>3</sub> , SiF <sub>3</sub>
ClF <sub>5</sub> /F <sub>2</sub>	0.3/3.0	125	O <sub>2</sub> , N <sub>2</sub>		O <sub>2</sub> , Cl <sub>2</sub>	
ClF <sub>5</sub> /F <sub>2</sub>	1.0/2.5	70	N <sub>2</sub> , O <sub>2</sub>	O <sub>2</sub> , N <sub>2</sub>	ClF <sub>2</sub> , ClO <sub>2</sub>	
ClF <sub>5</sub> /F <sub>2</sub>	1.7/4.9	300	N <sub>2</sub> , F <sub>2</sub>	F <sub>2</sub> , SiF <sub>3</sub>	ClO <sub>2</sub> , ClO <sub>3</sub>	
ClF <sub>5</sub> /F <sub>2</sub>	2.0/2.0	100	CO <sub>2</sub> , O <sub>2</sub>	O <sub>2</sub> , CO <sub>2</sub>	ClO <sub>2</sub> , Cl <sub>2</sub>	
ClF <sub>5</sub> /F <sub>2</sub>	0.5/2.6	200	F <sub>2</sub> , O <sub>2</sub>	O <sub>2</sub> , F <sub>2</sub>	ClF <sub>2</sub> , ClF <sub>4</sub>	SiF, ClF
ClF <sub>5</sub> /F <sub>2</sub>	1.8/3.0	200	F <sub>2</sub> , O <sub>2</sub>	F <sub>2</sub> , ClF <sub>2</sub>	ClF, ClF <sub>2</sub>	ClF <sub>2</sub> , ClF <sub>4</sub>
BrF <sub>5</sub> /F <sub>2</sub>	2.3/3.8	200	F <sub>2</sub> , O <sub>2</sub>	O <sub>2</sub> , F <sub>2</sub>	F <sub>2</sub> , BrF <sub>4</sub>	F <sub>2</sub> , BrF <sub>4</sub>
BrF <sub>5</sub> /F <sub>2</sub>	1.9/2.9	200	F <sub>2</sub> , O <sub>2</sub>	SiF <sub>3</sub> , O <sub>2</sub>	O <sub>2</sub> , F <sub>2</sub>	F <sub>2</sub> , BrF <sub>4</sub>
NF <sub>3</sub> /ClF <sub>5</sub>	2.2/2.1	100	NF <sub>2</sub> , NF <sub>3</sub>	NF <sub>2</sub> , F <sub>2</sub>	F <sub>2</sub> , ClF <sub>2</sub>	CO <sub>2</sub> , Cl <sub>2</sub>
NF <sub>3</sub>	neat	50	NF <sub>2</sub> , NF	NF <sub>2</sub> , NF	NF <sub>2</sub> , NF	
NF <sub>3</sub> /ClF <sub>5</sub>	1.1/1.1	200	NF <sub>2</sub> , NF	NF <sub>2</sub> , NF	ClF <sub>2</sub> , ClF <sub>4</sub>	ClF, Cl
NF <sub>3</sub> /ClF <sub>5</sub>	1.6/0.8	150	NF <sub>2</sub> , NF	NF <sub>2</sub> , NF <sub>3</sub>	ClF <sub>2</sub> , ClF <sub>4</sub>	NF <sub>2</sub> , ClF
NF <sub>3</sub> /ClF <sub>5</sub> /F <sub>2</sub>	0.8/0.6/1.6	100	NF <sub>2</sub> , F <sub>2</sub>	NF <sub>2</sub> , NF	ClF <sub>2</sub> , ClF <sub>4</sub>	
NF <sub>3</sub> /ClF <sub>5</sub>	3.0/1.8	200	NF <sub>2</sub> , NF	NF <sub>2</sub> , NF	ClF <sub>2</sub> , ClF <sub>4</sub>	ClF <sub>2</sub> , ClF
NF <sub>3</sub> /ClF <sub>5</sub>	1.3/0.8	200	NF <sub>2</sub> , NF	NF <sub>2</sub> , NF	NF <sub>2</sub> , NF	ClF, ClO <sub>2</sub>

\*Table entries are neutral species corresponding to cations of appropriate M/E valves.

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